Reaction of Ketene with Ethyl Acetoacetate in the Presence of Pyridine

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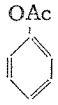
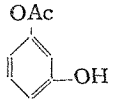
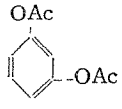
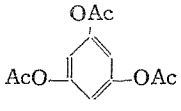
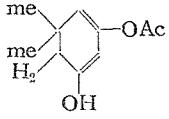
rivatives were produced.

(3) In the reactions with their sodium salts, O-acetyl derivatives were produced, containing a small amount of C-acetyl derivatives.

Some experimental results were cited in Tables 1 and 2.

Table 2. Some physical constants of O-acetyl derivatives obtained from phenol, resorcine, phloroglucine and dimedone.

O-acetyl derivative	Physical properties		
	m.p. (°C)	b.p. (°C)	n_D^{20}
	—	111 (60 mm.)	1.5200
	—	135-7 (7 mm.)	1.5328
	—	130-1 (7 mm.)	1.5034
	105-7	—	—
	—	128-132 (15 mm.)	1.4814

Reaction of Ketene with Ethyl Acetoacetate in the Presence of Pyridine

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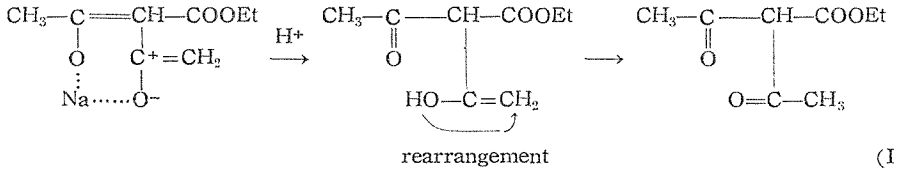
In the presence of a very small amount of pyridine, ketene was reacted with ethyl acetoacetate above -20°C, and a reaction product rich in O-acetyl- (II), poor in C-acetyl ethyl acetoacetate (I), was obtained.

* 礒 島 敏 三

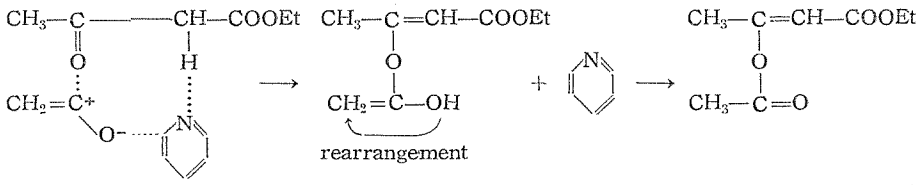
On the other hand, when an equimolar amount of pyridine was used above -40°C, O-acetyl derivative was a sole product, no C-acetyl derivative being formed.

A mechanism of the formation of C-acetyl derivative in the reaction[1] of ketene with sodium salt of ethyl acetoacetate is probably as follows:



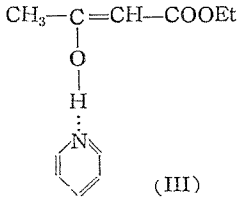
(I)

The formation of O-acetyl derivative in the presence of pyridine may occur through following mechanism.

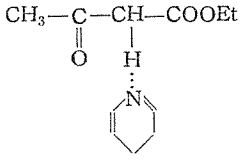


(II)

The author anticipates the presences of H-bonding (III) or (IV) between ethyl acetoacetate and pyridine. The H-bonding (III), however, was denied by Le Fèvre[2].

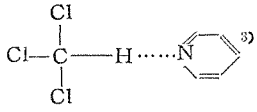


(III)

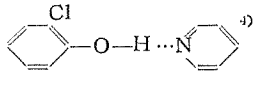


(IV)

Though the presence of H-bonding (IV) has not yet been confirmed, it is quite probable, taking into account that the H-bonding in



and in



was already proved, and pK_A values of *O*-chlorophnol ($pK_A = 10-11$) and ethyl acetoacetate ($pK_A = 10.7$)[5] are almost equal.

REFERENCES

(1) T.Isoshima, This Bulletin, **31**, 382 (1953).

(2) Le Fèvre, *J. Chem. Soc.*, **1949**, 2230.
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(5) R.P.Bell, *Trans. Faraday Soc.*, **39**, 253 (1943).